

# Calorimetric studies on $\text{Se}_{0.68}\text{Ge}_{0.22}\text{M}_{0.10}$ ( $\text{M} = \text{Cd}, \text{In}, \text{Pb}$ ) Chalcogenide Glasses

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## Abstract

Differential scanning calorimetry (DSC) is performed at different heating rates under non-isothermal conditions to calculate the activation energy of crystallization  $E_c$  for chalcogenide glasses  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{M}_{0.10}$  ( $\text{M} = \text{Cd}, \text{In}$  and  $\text{Pb}$ ) using the well known Kissinger's relation, Matusita-Sakka theory and the method of Augis-Bennett.

The overall mean bond energy  $\langle E \rangle$  of these glassy alloys has been evaluated using theory of Tichy and Ticha. A good correlation has been found between  $E_c$  and  $\langle E \rangle$ . This indicates that the overall mean bond energy plays an important role in the thermal crystallization of chalcogenide glasses.

**Key Words:** Chalcogenide glasses, Differential Scanning Calorimetry, Activation energy of crystallization.

## 1. Introduction

Investigations of physical properties in chalcogenide glasses gained much importance because of their potential technological applications. On the basis of various physical properties, covalently bonded chalcogenide glasses have been classified into two main categories:

Ge type, which includes tetrahedral coordinated substances, such as a-Ge, a-Si and III-IV compounds.

Se type, which includes the chalcogen elements (Se, Te, S) and their multicomponent alloys.

The  $\text{Se}_x\text{Ge}_{1-x}$  system is expected to fall into either category depending upon the value of  $x$ . These glasses have, therefore, been widely studied. Due to their wide composition range [1] and the fact that bulk glasses are easily obtained,  $\text{Se}_x\text{Ge}_{1-x}$  system has become an ideal system to investigate a great variety of properties and their correlation with structure and composition. Tohge et al. were the first to point out the role of Pb [2] and Bi [3] modifiers in the appearance of n-type conduction in Se-Ge glasses. Since then, ternary glass systems based on Se-Ge binary system has gained much importance.

In recent years, effort is being made to develop chalcogenide-based erasable optical storage media. The study of crystallization kinetics is one of the most important issues in developing phase change materials. The crystallization kinetics in chalcogenide glasses has, therefore, been investigated by various workers using isothermal and non-isothermal methods [4-11].

The present paper reports the crystallization kinetic studies of ternary glassy  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{M}_{0.10}$  ( $\text{M} = \text{Cd, In, Pb}$ ) system. Some other important studies (X-ray spectroscopic studies, dielectric studies and space charge limited conduction measurements) have already been reported on these materials in a series of papers [12-14] by our group in past.

The most widely used theory for interpreting the isothermal crystallization kinetics of amorphous materials is that of Johnson–Mehl–Avrami (JMA). This equation associated with the theory expresses the extent of crystallization  $\alpha$  as a function of time viz the volume fraction crystallized at a particular time. Although isothermal transformations are theoretically simpler, it is difficult to obtain a truly isothermal experiment as phase changes can occur during the non-isothermal heating period prior to the isothermal segment. Unfortunately, difficulties exist in describing the kinetics of a non-isothermal process due to the temperature dependence of both nucleation and growth rates. Several well-known methods have been developed to determine the crystallization parameters in non-isothermal crystallization processes, such as the Kissinger’s method [15], Matusita & Sakka theory [16, 17] and method of Augis and Bennett [18], all of which require multiple non-isothermal experiments in order to obtain kinetic parameters.

Three different methods of analysis (as described in the next section) have been used to study the crystallization kinetics of the above-mentioned glassy alloys under non-isothermal condition. Using DSC thermograms of these alloys, the values of activation energy of crystallization  $E_c$  have been determined by Kissinger’s method [15], Matusita & Sakka theory [16, 17] and the method of Augis and Bennett [18]. The overall mean bond energy  $\langle E \rangle$  of these alloys has been evaluated using the theory developed by Tichy and Ticha. A good correlation has been found between  $E_c$  and  $\langle E \rangle$ .

## 2. Details of Non-isothermal Methods Used

The crystallization kinetics of amorphous alloys has been intensively studied in the past using the classical Johnson-Mehl-Avrami (JMA) theoretical model in which the crystallization fraction  $\alpha$  can be described as a function of time  $t$  according to the formula

$$\alpha(t) = 1 - \exp[-(Kt)^n] \quad (1)$$

where  $n$  is the Avrami index and  $K$  is the rate constant and is given by

$$K = K_o \exp(-E_c/RT). \quad (2)$$

Here,  $E_c$  is the activation energy of crystallization,  $R$  is the universal gas constant and  $K_o$  is also a constant.

Based on JMA model, different authors have developed very diverse methods to study the amorphous to crystalline (a-c) transformation of glassy alloys. Given below are the details of three important and useful methods, which have been used in the present study.

### 2.1. Kissinger’s relation

According to Kissinger [15], peak temperature of crystallization  $T_c$  can be expressed in terms of the heating rate  $\beta$  as

$$\ln(\beta/T_c^2) = -E_c/RT_c + \text{constant}. \quad (3)$$

This equation is used to calculate the activation energy of crystallization by plotting the curve  $\ln \beta / T_c^2$  vs.  $1/T_c$ .

## 2.2. Matusita-Sakka theory

The extent of crystallization  $\alpha$  at a temperature  $T$  is well expressed by the expression

$$\ln(1 - \alpha)^{-1} = (C/\beta^n) \cdot [(-nE_c)/RT] \quad (4)$$

derived by Matusita and Sakka [16, 17] from the classical JMA equation.

Further, since the values of  $\alpha$  are independent of  $\beta$  at  $T = T_c$  [19], so at  $T = T_c$ , equation (4) takes the form

$$\ln\beta = -E_c/RT_c + \text{constant} \quad (5)$$

This equation is used to calculate the activation energy of crystallization by plotting the curve  $\ln \beta$  vs.  $1 / T_c$ .

## 2.3. Method of Augis-Bennett

The activation energy of crystallization  $E_c$  can also be determined by an approximation method developed by Augis and Bennett [18]. The relation used by them is of the form

$$\ln\beta/T_c = -E_c/RT_c + \ln K_o. \quad (6)$$

The activation energy of crystallization can be evaluated by this equation using the plots of  $\ln \beta / T_c$  against  $1 / T_c$ .

## 3. Experimental

Glassy alloys of  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{M}_{0.10}$  ( $M = \text{Cd, In and Pb}$ ) were prepared via the technique of quenching. The exact proportions of high purity (99.999%) elements, in accordance with their atomic fractions, were weighed using a Shimadzu/Libror AEG-120 electronic balance with accuracy to  $2 \times 10^{-4}$  gm. The materials were then sealed in evacuated ( $\sim 10^{-5}$  Torr) quartz ampoules (length  $\sim 5$  cm and internal diameter  $\sim 8$  mm). Each ampoule was kept inside the furnace at 1000 °C (where the temperature was raised at a rate of 3–4 °C/min.). To obtain homogeneous glassy alloys, all the ampoules were constantly rocked during heating, by a rotating ceramic rod to which the ampoules were attached in the furnace.

After rocking for about 12 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropped into ice-cooled water. The ingots of the samples were then taken out by breaking the quartz ampoules.

The glasses, thus prepared, were ground to make fine powder for DSC studies. This technique is particularly important due to the fact that: (1) it is easy to carry out; (2) it requires little sample preparation; (3) it is quite sensitive; and (4) it is relatively independent of the sample geometry.

10 to 20 mg of each sample was heated at a constant heating rate and the changes in heat flow with respect to an empty pan were measured. Five heating rates (5, 10, 15, 20 and 25 °C/ min) were chosen in the present study.

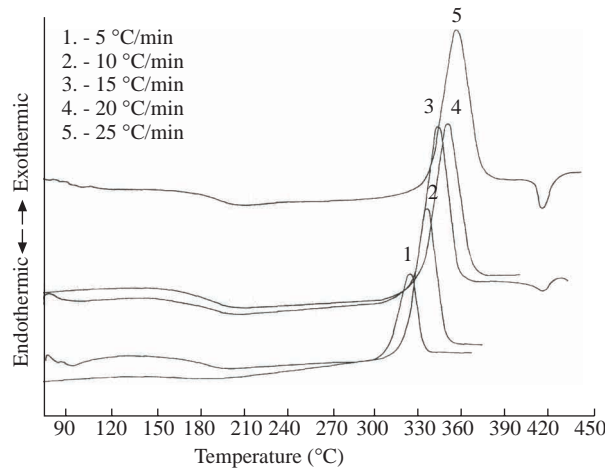
## 4. Results

Figure 1 shows the typical DSC thermograms for ternary alloy  $\text{Se}_{0.68}\text{Ge}_{0.20}\text{Pb}_{0.10}$  at different heating rates. Similar thermograms were obtained for other glassy alloys (not shown here). The temperature

corresponding to exothermic peak in the DSC scan is taken at the peak crystallization temperature  $T_c$ . The values of peak crystallization temperature  $T_c$  at different heating rates for these glassy alloys are given in Table 1.

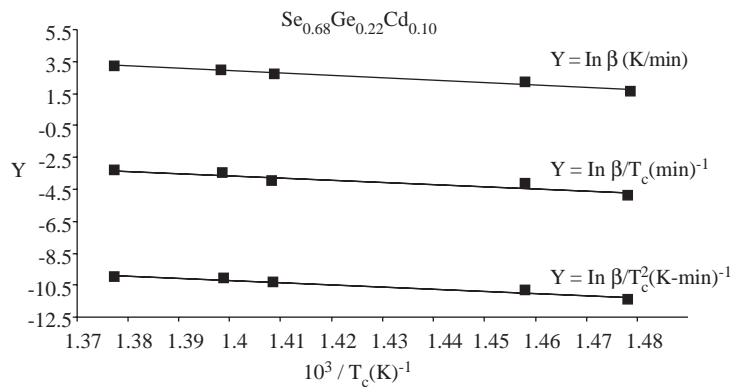
**Table 1.** Peak crystallization temperatures of glassy  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{M}_{0.10}$  (M = Cd, In, Pb) alloys at different heating rates.

Sample	$T_c$ (°C)				
	5 °C/min	10 °C/min	15 °C/min	20 °C/min	25 °C/min
$\text{Se}_{0.68}\text{Ge}_{0.22}\text{Cd}_{0.10}$	403.5	413.0	437.0	442.0	453.0
$\text{Se}_{0.68}\text{Ge}_{0.22}\text{In}_{0.10}$	386.0	401.0	412.0	423.0	430.0
$\text{Se}_{0.68}\text{Ge}_{0.22}\text{Pb}_{0.10}$	324.0	337.5	346.5	352.5	358.5

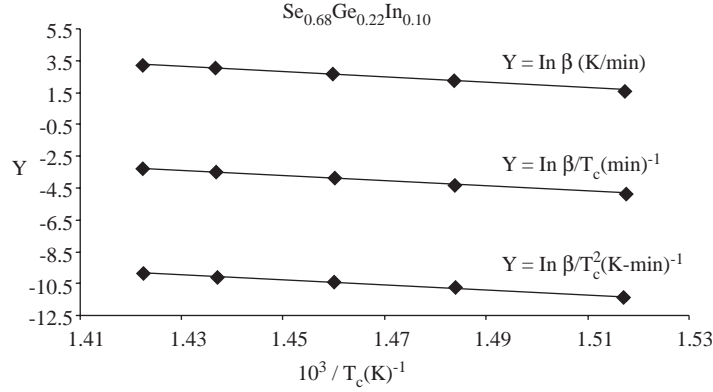


**Figure 1.** DSC Thermograms for glassy  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{Pb}_{0.10}$  alloy at different heating rates.

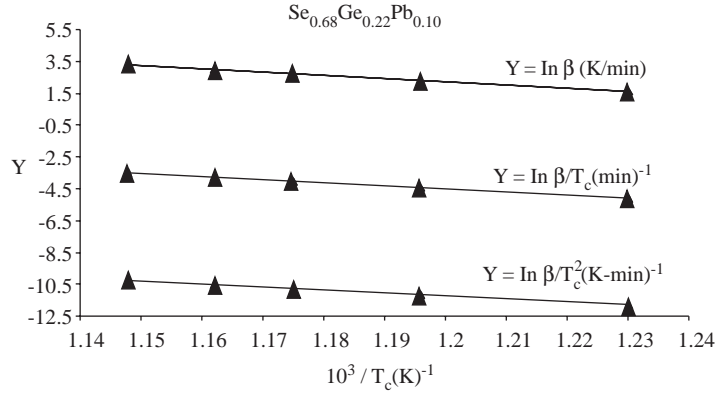
Following the three methods described in section 2, the plots of  $\ln(\beta / T_c^2)$ ,  $\ln \beta$  and  $\ln(\beta / T_c)$  against  $10^3 / T_c$  were obtained for the glassy  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{M}_{0.10}$  alloys (M = Cd, In, Pb). These plots were found to be straight lines. The plots are shown in Figures 2-4 for these alloys.



**Figure 2.** Plots of  $\ln \beta$ ,  $\ln \beta/T_c$ ,  $\ln \beta/T_c^2$  against  $10^3 / T_c$  for glassy  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{Cd}_{0.10}$  alloy.



**Figure 3.** Plots of  $\ln \beta$ ,  $\ln \beta/T_c$ ,  $\ln \beta/T_c^2$  against  $10^3 / T_c$  for glassy  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{In}_{0.10}$  alloy.



**Figure 4.** Plots of  $\ln \beta$ ,  $\ln \beta/T_c$ ,  $\ln \beta/T_c^2$  against  $10^3 / T_c$  for glassy  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{Pb}_{0.10}$  alloy.

The values of  $E_c$  for all the three alloys are given in Table 2. Comparison of  $E_c$  values of different alloys obtained from equations (3), (5) and (6) shows that the values are in good agreement with each other. This means that one can use any of the three equations to calculate the activation energy of crystallization.

**Table 2.** Activation energy of crystallization  $E_c$  for different glassy alloys.

Sample	$E_C$ (eV)		
	Equation (3)	Equation (5)	Equation (6)
$\text{Se}_{0.68}\text{Ge}_{0.22}\text{Cd}_{0.10}$	1.14	1.26	1.20
$\text{Se}_{0.68}\text{Ge}_{0.22}\text{In}_{0.10}$	1.32	1.44	1.38
$\text{Se}_{0.68}\text{Ge}_{0.22}\text{Pb}_{0.10}$	1.41	1.51	1.46

## 5. Discussion

The activation energy of crystallization  $E_c$  in ternary alloys  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{M}_{0.10}$  ( $\text{M} = \text{Cd}, \text{In}, \text{Pb}$ ) has been found to be increasing in the order  $(E_c)_{\text{Cd}} < (E_c)_{\text{In}} < (E_c)_{\text{Pb}}$ . This increasing sequence of  $E_c$  can be explained in terms of overall mean bond energy  $\langle E \rangle$  of these alloys. Values of the overall mean bond energy  $\langle E \rangle$  for any glassy alloys, which were found to depend on  $\langle Z \rangle$ , the degree of cross-linking per atom  $P_r$ , the type of bonds and the bond energy forming a network can be evaluated as described by Tichy and Ticha [20].

The average coordination number  $\langle Z \rangle$  of the studied glasses were evaluated using the standard procedure described by Tanaka [21], using coordination numbers (CN) of 4, 4 and 2 for M ( $\text{M} = \text{Cd}, \text{In},$

Pb), Ge and Se, respectively. Thus, for the glassy system  $\text{Ge}_a\text{M}_b\text{Se}_c$  ( $a + b + c = 1$ ), the values of  $\langle Z \rangle$  could be given by the following relation:

$$\langle Z \rangle = (aZ_{\text{Ge}} + bZ_{\text{M}} + cZ_{\text{Se}})/(a + b + c), \quad (7)$$

where  $Z_{\text{Se}}$ ,  $Z_{\text{Ge}}$  and  $Z_{\text{M}}$  are the co-ordination numbers of Se, Ge and metallic additive M ( $\text{M} = \text{Cd}, \text{In}, \text{Pb}$ ), respectively, in  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{M}_{0.10}$  systems under study.

The bond energies  $E_{AB}$  of hetropolar A-B bonds can be, in first approximation, estimated using Pauling's relation [22]:

$$E_{AB} = 0.5(E_{A-A} + E_{B-B}) + 23(\chi_A - \chi_B)^2, \quad (8)$$

where  $E_{A-A}$  and  $E_{B-B}$ , and  $\chi_A$  and  $\chi_B$  are, respectively, homopolar bond energies and electronegativity for A and B atoms. The homopolar bond energies and electronegativity are obtained from [23].

The degree of cross-linking per atom for chalcogen-rich region, as in the present case, can be expressed as

$$P_r = (aZ_{\text{Ge}} + bZ_{\text{M}})/(a + b + c) \quad (9)$$

The mean bond energy of average cross-linking per atom ( $E_{cl}$ ) is given by

$$E_{cl} = P_r \cdot E_{hb}, \quad (10)$$

where the average hetropolar bond energy is given by

$$E_{hb} = [aZ_{\text{Ge}}E_{\text{Ge-Se}} + bZ_{\text{M}}E_{\text{M-Se}}]/[aZ_{\text{Ge}} + bZ_{\text{M}}], \quad (11)$$

where  $E_{\text{Ge-Se}}$  and  $E_{\text{M-Se}}$  are the hetropolar bond energies of Ge-Se and M-Se hetropolar bonds. The average bond energy per atom of the "remaining matrix"  $E_{rm}$  is defined as

$$E_{rm} = 2(0.5 \langle Z \rangle - P_r)E_{\text{Se-Se}} / \langle Z \rangle. \quad (12)$$

Here,  $E_{\text{Se-Se}} = (E_{\text{Ge-Ge}} + E_{\text{M-M}} + E_{\text{Ge-M}})/3$  is the homopolar bond energy of a 'Se - Se' bond in the chalcogen-rich region.

Finally, the overall mean bond energy is given by

$$\langle E \rangle = E_{cl} + E_{rm}. \quad (13)$$

The values of the overall mean bond energy for the glassy alloys  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{M}_{0.10}$  ( $\text{M} = \text{Cd}, \text{In}, \text{Pb}$ ) are given in Table 3. From this table, it is clear that the overall mean bond energy  $\langle E \rangle$  for these glassy alloys has also the same increasing order as  $E_c$ .

**Table 3.** Overall mean bond energy  $\langle E \rangle$  for different glassy alloys.

Sample	$\langle E \rangle$ (eV)
$\text{Se}_{0.68}\text{Ge}_{0.22}\text{Cd}_{0.10}$	6.30
$\text{Se}_{0.68}\text{Ge}_{0.22}\text{In}_{0.10}$	6.50
$\text{Se}_{0.68}\text{Ge}_{0.22}\text{Pb}_{0.10}$	6.70

It is well known that the activation energy of crystallization is associated with the nucleation and growth process that dominates the devitrification of most glassy solids [24, 25]. The increasing sequence of  $E_c$  in ternary alloys  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{M}_{0.10}$  ( $\text{M} = \text{Cd}, \text{In}, \text{Pb}$ ) may, therefore, be associated with the nucleation and growth process which requires more energy due to increase in the overall mean bond energy in the sequence  $(\langle E \rangle)_{\text{Cd}} < (\langle E \rangle)_{\text{In}} < (\langle E \rangle)_{\text{Pb}}$  due to addition of the metallic additives. The plot of  $E_c$  vs.  $\langle E \rangle$  is shown in Figure 5. It is clear from this figure that  $E_c$  depends upon overall mean bond energy in the present glass systems.

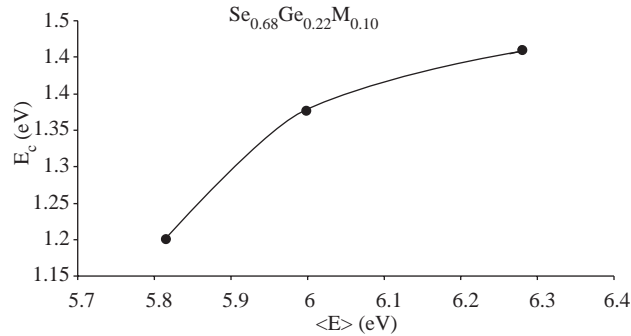


Figure 5. Plot of  $E_c$  vs.  $\langle E \rangle$  for glassy  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{M}_{0.10}$  system.

## 6. Conclusion

The calorimetric measurements have been performed in glassy alloys  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{M}_{0.10}$  ( $\text{M} = \text{Cd}, \text{In}, \text{Pb}$ ). DSC technique has been used in the present study to calculate the activation energy of crystallization  $E_c$ . Values of  $E_c$  obtained by three different methods are found to be in good agreement with each other.

The overall mean bond energy  $\langle E \rangle$  of these glassy alloys has been evaluated using theory of Tichy and Ticha. The activation energy of crystallization in ternary alloys  $\text{Se}_{0.68}\text{Ge}_{0.22}\text{M}_{0.10}$  ( $\text{M} = \text{Cd}, \text{In}, \text{Pb}$ ) has been found to increase with mean bond energies of these alloys. This indicates that the overall mean bond energy plays an important role in the thermal crystallization of chalcogenide glasses.

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